

JAPANESE

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Representative draw

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

(71)Applicant : JSR CORP

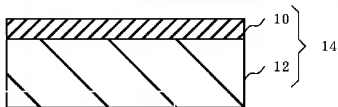
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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Application of the Invention]This invention relates to an activity energy-line hardenability resin composition (a hardenability resin composition may only be called.), transparency and the hardening layer of a low refractive index excellent in radiation-curing nature or spreading nature, and an antireflection film with low reflectance which hardens a hardenability resin composition on a substrate.

[0002]

[Description of the Prior Art]The fluorine system compound and the fluoro-resin constituent are used using the point which is a low refractive index as optical adhesives, such as charges of light-reflection-prevention film material, such as an optical lens, a film, and glass for CRT, a charge of clad plate material of an optical fiber, or an optical fiber, an optical lens. Since a fluorine compound has water repellence and oil repellency, it is used also as antifouling coat material.

[0003]One of such the fluoro-resin constituents is indicated by JP,64-14221,A. This fluorine system constituent to the fluorine-containing copolymer which consists of an acrylate monomer which has a **alpha-fluoro acrylate monomer and a glycidyl group. It comprises ten to compound 90 weight section produced by reacting a carboxyl-group-containing-ethylene nature unsaturation monomer, ten to acrylic system monomer 90 weight section for ** viscosity control, and 0.05 to ** photopolymerization initiator 20 weight section.

[0004]The fluoro-resin constituent which comprised a fluorine polymer which consists of an alpha-fluoro acrylate monomer and the other acrylate monomer, an alpha-fluoro acrylate monomer, and other acrylic system monomers is indicated by JP,62-250047,A. The fluoro-resin

constituent in which the fluorine atom comprised 30% of the weight or more of a fluorine polymer, an alpha-fluoro acrylate monomer, other acrylic system monomers, and polyfunctional monomer is indicated by JP,62-199643,A.

[0005]

[Problem(s) to be Solved by the Invention]However, the fluororesin constituent indicated by which Patent Gazette was also lacking in the compatibility between alpha-fluoro acrylate monomer and a fluorine polymer, and difficult to form the hardening layer which has uniform thickness, and the hardening layer excellent in transparency. The fluororesin constituent indicated by which Patent Gazette was also deficient in the adhesion power to the surface slidability, the substrate, especially glass, and polycarbonate in a hardening layer after hardening, and difficult to use it for the use as the charge of antireflection film material, and a charge of clad plate material of an optical fiber.

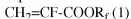
[0006]On the other hand, in JP,62-250047,A etc., adding a silane coupling agent and a low-molecular-weight siloxane compound in a fluororesin constituent is also proposed in order to raise adhesion power with a substrate. However, since silane coupling agents were lacking in compatibility with a fluorine system copolymer or alpha-fluoro acrylate monomer, the problem of it having become still more difficult to obtain a uniform hardening layer, or being easy to carry out bleeding of the silane coupling agent etc. from a hardening layer was seen. The problem of it exfoliating easily, if silicone series resin is used in an oil, and its pot life being short, a refractive index being still higher, and the use range being limited conventionally, was pointed out as JP,62-250047,A etc. were indicated.

[0007]Then, the hexafluoropropylene copolymer which includes a siloxane bond even if it is a non-solvent when this invention person takes lessons from the above-mentioned problem and it inquires wholeheartedly. When alpha-fluoro acrylate monomer showed the specifically outstanding compatibility and moreover combined in this way, it found out that the adhesion power to a substrate improved. It found out not producing problems, such as pot life in conventional silicone series resin, either, making use of the characteristic of a siloxane bond (silicone), since it is not what uses silicone series resin alone. That is, an object of this invention is to provide the activity energy-line hardenability resin composition in which the spreading nature which was excellent even if it was a non-solvent, and compatibility are shown. Another purpose of this invention aims at providing the hardening layer (antireflection film) which has a low refractive index and reflectance, while excelling in the transparency and adhesion which consist of a hardenability resin composition.

[0008]

[Means for Solving the Problem]This invention is an activity energy-line hardenability resin composition containing a hexafluoropropylene copolymer including a siloxane bond and alpha-fluoro acrylate monomer. Even if it is a non-solvent by constituting in this way, when outstanding compatibility and spreading nature are obtained and a hardening layer is formed, it can be stabilized and outstanding adhesion and transparency can be made to reveal. Since a siloxane bond is introduced in a hexafluoropropylene copolymer, problems by a siloxane compound, such as a fall of pot life and bleeding, are effectively avoidable.

[0009]In constituting a hardenability resin composition of this invention, it is preferred to contain alpha-fluoro acrylate monomer expressed with a following general formula (1).



R_f is a hydrocarbon group which may contain an oxygen atom and

which has at least one fluorine atom among [general formula (1).] If it is such a monofunctional monomer, compatibility more outstanding between hexafluoropropylene copolymers including a siloxane bond is acquired, and when it is made to harden, a hardening layer excellent in transparency can be formed.

[0010]In constituting a hardenability resin composition of this invention, it is preferred that a hexafluoropropylene copolymer including a siloxane bond is a copolymer obtained using an azo content polysiloxane compound as a radical generator. By constituting in this way, a hexafluoropropylene copolymer including a siloxane bond can be obtained for easy and a short time, and a cheap hardenability resin composition can be provided. A siloxane bond which was carried out in this way and introduced is blocked, and can reveal more outstanding surface slidability in a hardening layer.

[0011]In constituting a hardenability resin composition of this invention, it is preferred that a hexafluoropropylene copolymer including a siloxane bond is a copolymer obtained using a nonionic reactive emulsifier. By constituting in this way, compatibility of a hexafluoropropylene copolymer including a siloxane bond and alpha-fluoro acrylate monomer can be made still better.

[0012]In constituting a hardenability resin composition of this invention, it is preferred to make into 20-70-mol% of value within the limits hexafluoropropylene unit quantity of hexafluoropropylene copolymer 100 mol % Naka including a siloxane bond. While water repellence and low-refractive-index nature outstanding by constituting in this way are obtained, alpha-fluoro acrylate monomer is more mixable to homogeneity to a hexafluoropropylene copolymer.

[0013]In constituting a hardenability resin composition of this invention, it is preferred to make an addition of alpha-fluoro acrylate monomer into a value of one to 10,000 weight section within the limits to hexafluoropropylene copolymer 100 weight section including a siloxane bond. By constituting in this way, alpha-fluoro acrylate monomer is more mixable to homogeneity to a hexafluoropropylene copolymer including a siloxane bond.

[0014]Another mode of this invention is a hardening layer which shifts and hardens that hardenability resin composition with an activity energy line to mention above, or an antireflection film hardened with an activity energy line on a substrate. By constituting in this way, it has outstanding adhesion over a substrate, and the outstanding surface slidability, and an antireflection film etc. which have the acid resistibility which moreover adjusted a refractive index easily and was excellent can be obtained.

[0015]

[Embodiment of the Invention]Hereafter, the embodiment about the activity energy-line hardenability resin composition of this invention and an antireflection film is described concretely.

[0016][A 1st embodiment] The hexafluoropropylene copolymer (a hexafluoropropylene copolymer may only be called hereafter.) in which a 1st embodiment includes a siloxane bond, It is an activity energy-line

hardenability resin composition containing alpha-fluoro acrylate monomer expressed with a following general formula (1), and a radiation-initiated-polymerization initiator. And this hexafluoropropylene copolymer is a copolymer obtained using the azo content polysiloxane compound and the nonionic reactive emulsifier. $\text{CH}_2=\text{CF}-\text{COOR}_f$ (1)

R_f is a hydrocarbon group which may contain an oxygen atom and which has at least one fluorine atom among [general formula (1).] [0017](1) A hexafluoropropylene copolymer including a hexafluoropropylene copolymer siloxane bond including a siloxane bond, Hexafluoropropylene, the hexafluoropropylene concerned, a copolymerizable monomer (a copolymerization monomer may only be called.), and a siloxane component can be obtained copolymerization or by making it react. Here, the copolymerization monomer is used in addition to hexafluoropropylene in order to be because it is difficult to polymerize and to adjust the fluorine contents in a copolymer, etc. in a hexafluoropropylene simple substance. The siloxane components in a 1st embodiment are some azo content polysiloxane compounds as a radical polymerization initiator.

[0018]** hexafluoropropylene and a copolymerizable monomer -- as a kind of copolymerizable monomer, 2-hydroxyethyl vinyl ether, 3-hydroxypropyl vinyl ether, 2-hydroxypropyl vinyl ether, 4-hydroxybutyl vinyl ether, 3-hydroxybutylvinyl ether, 5-hydroxypentylvinyl ether, Hydroxyl group containing vinyl ether, such as 6-hydroxyhexylvinyl ether; 2-hydroxyethyl allyl ether, Hydroxyl group content allyl ether; allyl alcohol, such as 4-hydroxybutyl allyl ether and glycerol monoallyl ether; The methyl vinyl ether, Ethyl vinyl ether, n-propylvinyl ether, isopropylvinyl ether, n-butylvinyl ether, isobutylvinyl ether, tert-butylvinyl ether, n-pentylvinyl ether, n-hexylvinyl ether, n-octylvinyl ether, Alkyl vinyl ether or cycloalkyl vinyl ether, such as n-dodecylvinyl ether, 2-ethylhexyl vinyl ether, and cyclohexylvinyl ether; Perfluoro (methyl vinyl ether), Perfluoro (ethyl vinyl ether), perfluoro (propylvinyl ether), Perfluoro (butylvinyl ether), perfluoro (isobutylvinyl ether), Perfluoro (alkyl vinyl ether) or perfluoro (alkoxy alkyl vinyl ether), such as perfluoro (propoxypropylvinyl ether), Or vinyl ether or (fluoroalkoxy alkyl) vinyl ether expressed with $\text{CH}_2=\text{CH}-\text{O}-\text{R}_g$ (R_g shows the alkyl group or alkoxyalkyl group containing a fluorine atom) (fluoro alkyl); Vinylidene fluoride, Chlorotrifluoroethylene, 3,3,3-trifluoropropylene, Fluoroolefins, such as tetrafluoroethylene; Vinyl acetate, Vinyl propionate, butanoic acid vinyl, vinyl pivalate, caproic acid vinyl, Carboxylic acid vinyl ester, such as BASA tic acid vinyl and stearic acid vinyl; Alpha olefin; 2,2,2-trifluoroethyl (meta) acrylate, such as ethylene, propylene, and isobutene, 2,2,3,3,3-pentafluoro propyl (meta) acrylate, 2-(perfluoro butyl) ethyl (meta) acrylate, 2-(perfluoro hexyl) ethyl (meta) acrylate, Fluoride content (meta) acrylic ester, such as 2-(perfluoro octyl) ethyl (meta) acrylate and 2-(perfluoro decyl) ethyl (meta) acrylate; Methyl (meta) acrylate, Ethyl (meta) acrylate, n-butyl (meta) acrylate, isobutyl (meta) acrylate, 2-methoxy ethyl (meta) acrylate, 2-ethoxyethyl (meta) acrylate, Acrylic ester (meta), such as 2-(n-propoxy) ethyl (meta) acrylate; (meta) Acrylic acid, Crotonic acid, maleic acid, fumaric acid, itaconic acid, allyl glycidyl ether, A carboxyl group or epoxy group content vinyl monomers, such as glycidyl (meta) acrylate; kind independent, such as N-vinyl monomers, such as N-vinyl

pyrrolidone and N-vinylcaprolactam, or two or more sorts of combination are mentioned.

[0019] In order to raise the yield of a hexafluoropropylene copolymer more among these copolymerization monomers, it is preferred to use hydroxyl group containing vinyl ether, alkyl vinyl ether, cycloalkyl vinyl ether, and carboxylic acid vinyl ester. In order to raise the fluorine contents of a hexafluoropropylene copolymer, it is preferred to use low-molecular-weight monomers, such as the methyl vinyl ether, ethyl vinyl ether, n-propylvinyl ether, isopropylvinyl ether, vinyl acetate, vinyl propionate, butanoic acid vinyl, and vinyl pivalate. In order for a hexafluoropropylene copolymer to high-hardness-ize, it is preferred to use branched state monomers, such as isopropylvinyl ether, tert-butylvinyl ether, and vinyl pivalate.

[0020] When the amount of hexafluoropropylene will be less than 53 % of the weight, a copolymerization monomer, In order to raise fluorine contents, it is preferred that fluorine contents like perfluoro (alkyl vinyl ether) or perfluoro (alkoxy alkyl vinyl ether), for example, carry out copolymerization of the large fluorine-containing monomer. In order to improve adhesion with a substrate, it is preferred to use the reactant group content monomer (a reactant group content monomer is called hereafter.) containing at least one reactant group chosen from hydroxyl, an epoxy group, an amino group, and a carboxyl group.

[0021]** As a ratio of each monomer which constitutes the loadings hexafluoropropylene copolymer of a copolymerization monomer, When monomer entire volume at the time of creating a copolymer is made into 100-mol %, it is preferred to make a hexafluoropropylene unit into 20-70-mol% of value within the limits, and it is more preferred to consider it as 25-55-mol% of value within the limits. Conversely, when it says, it is preferred to make a copolymerization monomeric unit into 30-70-mol% of value within the limits, and it is more preferred to consider it as 25-55 mol % mol% of value within the limits. This reason is because the adhesion and water repellence of a hardening layer may fall if hexafluoropropylene loadings become smaller than 20-mol %, and is because the transparency of a hardening layer may fall or a mechanical strength may fall, if it becomes larger than 70-mol % on the other hand.

[0022] When a reactant group content monomer is blended and monomer entire volume at the time of creating a copolymer for the loadings is made into 100-mol %, it is preferred to consider it as 1-20-mol% of value within the limits, and it is more preferred to consider it as 3-15-mol% of value within the limits. This reason is because the intensity of the coat formed and the adhesion power to a substrate may decline if a reactant group content monomer will be less than [1 mol %], and is because the preservation stability of a paint may fall on the other hand if 20-mol % is exceeded.

[0023]** As fluorine contents in a fluorine-contents hexafluoropropylene copolymer, it is preferred to consider it as 40 % of the weight or more, and it is more preferred to consider it as 45% of the weight or more of a value. When these fluorine contents will be less than 40 % of the weight, it is because a refractive index may become large and the characteristic as an antireflection film or a clad plate may be unable to be demonstrated. The fluorine contents in a hexafluoropropylene copolymer can be measured using the alizarin complex method.

[0024]** It is preferred to make the number average molecular weight

of a number average molecular weight hexafluoropropylene copolymer into the value of 5,000-2,000,000 within the limits. This reason is because the mechanical strength of the hexafluoropropylene copolymer obtained may fall if a number average molecular weight is smaller than 5,000, and is because compatibility with alpha-fluoro acrylate monomer may fall on the other hand if 2,000,000 is exceeded. Therefore, it is more preferred to make the number average molecular weight of a hexafluoropropylene copolymer into the value of 30,000-1,000,000 within the limits.

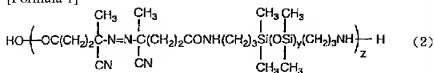
[0025]** Although not limited especially as a polymerization method of a polymerization method hexafluoropropylene copolymer, an emulsion polymerization method, a suspension polymerization method, a mass polymerization method, or a solution polymerization method can be taken, for example under existence of a radical polymerization initiator. This polymerization method can choose suitably a batch process, half-continuous system, or continuous system according to the purpose.

[0026](Azo content polysiloxane compound) The radical polymerization initiator used with such a polymerization method again, Although not restricted in particular, in order to introduce a siloxane bond easily in a hexafluoropropylene copolymer, the azo content polysiloxane compound is used by a 1st embodiment. The block copolymer which contains regularly the unit which consists of hexafluoropropylene and a copolymer component, and a polysiloxane unit, respectively can be easily created by using such a radical polymerization initiator. For example, if poly dimethylsiloxane uses the azo content polysiloxane compound connected by azo, the block copolymer of a hexafluoropropylene copolymer and poly dimethylsiloxane can be obtained.

[0027]VPS1001, VPS0501, etc. with which the poly dimethylsiloxane expressed with a general formula (2) was connected by azo as an azo content polysiloxane compound of such marketing, for example (all are the Wako Pure Chemical Industries, Ltd. make) are mentioned.

[0028]

[Formula 1]



[0029]y is an integer of 60-150 among [general formula (2), and z is an integer of 6-10.]

[0030]It is preferred to make the amount of azo content polysiloxane compound used into a value of 0.01 to 20 weight section within the limits to total quantity 100 weight section of hexafluoropropylene and its copolymerization monomer. If the amount of azo content polysiloxane compound used will be less than 0.01 weight sections, this reason, It is because a hexafluoropropylene copolymer may not be obtained and is because a molecular weight of a hexafluoropropylene copolymer obtained may fall remarkably on the other hand if the amount of azo content polysiloxane compound used exceeds 20 weight sections. Therefore, total quantity 100 weight section of hexafluoropropylene and its copolymerization monomer is received in the amount of azo content polysiloxane compound used from a viewpoint of such polymerization nature, It is more preferred to

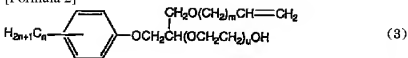
consider it as a value of 0.1 to 15 weight section within the limits, and it is still more preferred to consider it as a value of one to 10 weight section within the limits.

[0031](Other radical polymerization initiators) Radical polymerization initiators other than an azo content polysiloxane compound since a rate of polymerization is controlled in addition, For example, a kind independent of diacyl peroxide, ketone peroxides, hydroperoxide, dialkyl peroxide, peroxy ester species, an azo compound, and persulfate or two or more sorts of combination are mentioned. It is also preferred to use together organic reducing agents, such as inorganic reducing agents, such as sodium hydrogen sulfite and sodium pyrosulfite, cobalt naphthenate, and dimethylaniline, if needed. A quick radical reaction can be produced by using it, combining in this way. An iodine content fluorine compound can be used together with independence or organic peroxide mentioned above, an azo compound, or persulfate, and can be used conveniently.

[0032](Nonionic reactive emulsifier) By a 1st embodiment, it is characterized by using a nonionic reactive emulsifier in the case of a polymerization of a hexafluoropropylene copolymer again. This reason is for making still better compatibility of a hexafluoropropylene copolymer including a siloxane bond and alpha-fluoro acrylate monomer. As such a nonionic reactive emulsifier, an emulsifier expressed with a following general formula (3) can be mentioned, for example, and ADEKARIA soap NE-30 (made by Asahi Denka Kogyo K.K.) etc. is mentioned as a commercial nonionic reactive emulsifier.

[0033]

[Formula 2]



[0034]As for the integer of 1-20, and m, the integer of 1-10 and u of n are the integers of 10-100 among [general formula (3).]

[0035]It is preferred to make the amount of the nonionic reactive emulsifier used into the value of 0.01 to 15 weight section within the limits to total quantity 100 weight section of hexafluoropropylene and its copolymerization monomer. If the amount of the nonionic reactive emulsifier used will be less than 0.01 weight sections, this reason, It is because the addition effect may not be acquired and is because reprecipitation processing general to the fluorine-containing copolymer obtained when the amount of the nonionic reactive emulsifier used exceeds 15 weight sections may be performed and purification treatment may be impossible on the other hand. That is, when a nonionic reactive emulsifier exists so much, it is because it may become difficult to solidify a fluorine-containing copolymer. Therefore, it is more preferred to make the amount of the nonionic reactive emulsifier used into the value of 0.1 to 10 weight section within the limits to total quantity 100 weight section of hexafluoropropylene and its copolymerization monomer, and it is still more preferred to consider it as the value of one to 5 weight section within the limits.

[0036](2) alpha-fluoro acrylate monomer used for alpha-fluoro acrylate monomer ** kind this invention can use a large kind, without being restricted especially if it is acrylate which has a fluorine atom in alpha position. alpha-fluoro acrylate monomer can be specifically dissolved with a hexafluoropropylene copolymer. Even if alpha-fluoro acrylate

monomer is a case where it mixes with a hexafluoropropylene copolymer, radiation initiated polymerization is quickly possible for it, therefore by polymerizing can show a high glass transition point and an outstanding mechanical property. Such an alpha-fluoro acrylate monomer can be obtained with a manufacturing method (a methyl esterification reaction and an ester exchange reaction) indicated by JP,50-52019,A, for example.

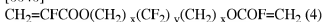
[0037]It is preferred that it is a compound expressed with a general formula (1) mentioned above as a desirable alpha-fluoro acrylate monomer. More specifically Trifluoroethyl alpha-fluoro acrylate, 2,2,3,3-tetrafluoro propyl alpha-fluoro acrylate, Kind independent, such as hexafluoro isopropyl alpha-fluoro acrylate, octafluoropentyl alpha-fluoro acrylate, and heptaecafluorodecyl alpha-fluoro acrylate, or two or more sorts of combination are mentioned.

[0038]That to which an oxygen atom intervened in R_f main chain in a general formula (1), for example, a compound expressed with a structural formula of $\text{CH}_2=\text{CF}-\text{COOCF}_2\text{C}(\text{CF}_3)\text{FOCF}(\text{CF}_3)_3$, is

preferred as an alpha-fluoro acrylate monomer. Thus, alpha-fluoro acrylate monomer to which an oxygen atom intervened into R_f main chain is because composition is comparatively easy and acquisition is easy.

[0039]It is preferred that it is also a divinyl compound expressed with the following general formula (4) and (5) as an alpha-fluoro acrylate monomer. By using such a divinyl compound, it is because a mechanical strength of a hardening layer obtained can be raised more.

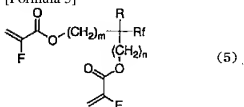
[0040]



1-2y of x are the integers of 4-12 among [general formula (4).]

[0041]

[Formula 3]



[0042]An integer (however, it does not become in 0 simultaneously.) to 0-10 and R of m and n are hydrogen or an alkyl group to the carbon numbers 1-10, and the contents as a general formula (1) with same R_f among [general formula (5).]

[0043]** It is preferred to make an addition and an addition of alpha-fluoro acrylate monomer into a value of one to 10,000 weight section within the limits to hexafluoropropylene copolymer 100 weight section. If an addition of alpha-fluoro acrylate monomer will be less than one weight section, this reason, It is because hardenability may fall remarkably and is because forming in desired thickness may become difficult since viscosity of a constituent will become low on the other hand if an addition of alpha-fluoro acrylate monomer exceeds 10,000 weight sections, or pliability and slidability of a hardening layer may fall. Therefore, since balance of hardenability or the characteristic of a hardening layer becomes better, hexafluoropropylene copolymer 100 weight section is received in an addition of alpha-fluoro acrylate

monomer, It is more preferred to consider it as a value of ten to 5,000 weight section within the limits, and it is more preferred to consider it as a value of 100 to 1,000 weight section within the limits.

[0044](3) A radiation-initiated-polymerization initiator hardenability resin composition can be made to be able to contain a radiation-initiated-polymerization initiator, and can be efficiently stiffened by irradiating with an activity energy line, for example, ultraviolet rays. That is, a radiation-initiated-polymerization initiator is a compound which promotes a polymerization reaction of alpha-fluoro acrylate monomer by receiving an activity energy line.

[0045]As an example of such a radiation-initiated-polymerization initiator, 1-hydroxycyclohexylphenyl ketone, A 2,2'-dimethoxy- 2-phenylacetophenone, xanthone, A fluorene, fluorenone, benzaldehyde, anthraquinone, a triphenylamine, Carbazole, 3-methylacetophenone, 4-chlorobenzo phenon, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, A Michler's ketone, benzoyl propyl ether, benzoin ethyl ether, Benzyl dimethyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-isobutane 1-one, 2-hydroxy-2-methyl-1-phenylpropan-1-one, a thioxan ton, Diethylthio xanthone, 2-isopropyl thioxan ton, 2-chloro thioxan ton, 2-methyl-1-[4-(methylthio) phenyl]-2-morpholinopropane 1-one, 2,4,6-trimethyl benzoyldiphenyl phosphine oxide, 2-benzyl-2-dimethylamino 1-(4-morpholinophenyl) butan-1-one, Kind independent, such as 1-[phenyl [4 -(2-hydroxyethoxy)-]]-2-hydroxy-isobutane 1-one, or two or more sorts of combination can be mentioned. 2,4,6-trimethyl benzoyldiphenyl phosphine oxide and 1-hydroxycyclohexylphenyl ketone are [among these] more preferred.

[0046]Although the amount in particular of radiation-initiated-polymerization initiator used is not restricted, either, it is preferred to consider it as a value of 0.1 to 20 weight section within the limits for example, when the total quantity of a hexafluoro copolymer and alpha-fluoro acrylate monomer is made into 100 weight sections. This reason is for reaction velocity of alpha-fluoro acrylate monomer becoming slow, or becoming easy to be influenced by oxygen etc. which exist in the circumference, when the amount of radiation-initiated-polymerization initiator used will be less than 0.1 weight sections. It is because a molecular weight of alpha-fluoro acrylate monomer may become low and a mechanical strength and heat resistance of a hardening layer which are obtained may fall on the other hand, if the amount of radiation-initiated-polymerization initiator used exceeds 20 weight sections. Therefore, since balance with reaction velocity of alpha-fluoro acrylate monomer, the characteristic of a hardening layer, etc. becomes better, it is more preferred to make the amount of radiation-initiated-polymerization initiator used into a value of 0.5 to 10 weight section within the limits.

[0047](4) To a constituent of additive agent this invention, it is also preferred to contain various kinds of additive agents for the purpose of an improvement of the spreading characteristic of the constituent concerned, the photosensitivity of the constituent concerned, the various characteristics of a hardening layer by the constituent concerned, etc. As such an additive agent, for example Polymeric materials other than a hexafluoropropylene copolymer, Colorant, such as paints and a color, a filler, an antioxidant, an ultraviolet ray absorbent, a SadamuMitsuyasu-ized agent, an antiaging agent, a silane coupling agent, a cross-linking compound, a surface-active agent, polymerization inhibitor, a solvent, etc. can be mentioned.

[0048] More specifically as a desirable polymeric material, acrylic resins, such as polymethyl (meta) acrylate, an epoxy resin, novolak resin, resole resin, etc. can be mentioned. As a desirable ultraviolet ray absorbent, a salicylic acid system ultraviolet ray absorbent, a benzophenone series ultraviolet ray absorbent, a benzotriazol system ultraviolet ray absorbent, a cyanoacrylate system ultraviolet ray absorbent, etc. can be mentioned. As a desirable antiaging agent, it is di-tert-butylphenol, pyrogallol, benzoquinone, hydroquinone, n-butylphenol, hydroquinone monopropyl ether, and 4 and 4'-[1,4-bis(4-hydroxyphenyl)-1-methylethyl]phenyl] Ethylidene] diphenol, 1,1,3-tris (2,5-dimethyl-4-hydroxyphenyl)-3-phenylpropane, diphenylamine, phenylenediamines, phenothiazin, mercaptobenzimidazole, etc. can be mentioned.

[0049] As a desirable silane coupling agent, gamma-aminopropyl triethoxysilane, gamma-mercapto propyltrimethoxysilane, gamma-methacryloxypropyltrimethoxysilane, etc. can be mentioned. It is still more preferred it to be preferred to consider it as a value of 0.01 to 5 weight section within the limits, respectively, and to make into a value of 0.01 to 3 weight section within the limits an addition of an additive agent mentioned above, when the total quantity of a hexafluoro copolymer and alpha-fluoro acrylate monomer is made into 100 weight sections. this reason is because the addition effect may not be revealed if an addition of various additive agents will be less than 0.01 weight sections, and is because the photoresist of a hardenability resin composition obtained may fall on the other hand if an addition of various additive agents exceeds five weight sections.

[0050] As a cross-linking compound, amino resin, such as melamine, polyisocyanate, An anhydride of polybasic acid and polybasic acid, polyamine, polyol, an epoxy compound, It is preferred to add combination beyond a kind or a NI kind out of compounds which have a cross-linking functional group and a basis in which a reaction is possible which constitute a polymer component, such as an epoxy resin and hydroxyl group-containing compound (for example, pentaerythritol, polyphenol, glycol). It is also preferred to carry out addition content of a cross-linking functional group of a polymer component and the reaction catalyst for promoting a reaction (crosslinking reaction) with a cross-linking compound into a constituent. Without spoiling an effect by this invention as an addition of a cross-linking compound, Since the suitable structure of cross linkage for a hardening layer formed from a hardenability resin composition can be introduced, it is preferred to consider it as a value within the limits of 0.5-1.0 Eq per Eq of cross-linking functional group which constitutes a polymer component, and it is still more preferred to consider it as a value within limits which are 0.7-1.0 Eq.

[0051] As for a surface-active agent, it is preferred to add for the purpose of raising the spreading characteristic and antistatic property of a hardenability resin composition etc. As such a surface-active agent, a surface-active agent with the publicly known anionic system surface-active agent, cation system surface-active agent, Nonion system surface-active agent, etc. can be mentioned. It is still more preferred it to be preferred to consider it as a value of 0.01 to 5 weight section within the limits, and to make an addition of a surface-active agent into a value of 0.01 to 3 weight section within the limits, when the total quantity of a hexafluoropropylene copolymer and alpha-fluoro acrylate monomer is made into 100 weight sections. this reason is because the addition effect

may not be revealed if an addition of a surface-active agent will be less than 0.01 weight sections, and is because the water resisting property of a hardenability resin composition and adhesion which are acquired may be spoiled on the other hand if an addition of a surface-active agent exceeds five weight sections.

[0052]It is preferred to add for the purpose of adjusting viscosity in a hardenability resin composition within desirable limits for a solvent, and raising spreading nature. As such a solvent, ethyl acetate, butyl acetate, isopropyl acetate, Ester species, such as isobutyl acetate and cellosolve acetate; Acetone, methyl ethyl ketone, Ketone, such as methyl isobutyl ketone and cyclohexanone; A tetrahydrofuran, Cyclic ether, such as dioxane; it is also preferred to be able to mention aromatic hydrocarbon, such as amide; toluene, such as N,N-dimethylformamide and N,N-dimethylacetamide, and xylene, and to use alcohols; aliphatic hydrocarbon with these.

[0053](5) A hardenability resin composition of hardenability resin composition ** preparing method this invention can be prepared by mixing with a hexafluoropropylene copolymer and alpha-fluoro acrylate monomer under a room temperature or heating conditions. Specifically, it can prepare easily using mixers, such as a mixer, a ball mill, and 3 rolls.

[0054]Viscosity of a viscosity hardenability resin composition ** A kind (monomer composition) and a molecular weight of a hexafluoropropylene copolymer, And it can adjust to a value within desirable limits which responded to a coating method to adopt a using rate of a hexafluoropropylene copolymer, and by setting up a viscosity controlling agent (a monomer component is included) suitably further. For example, it is preferred to adjust viscosity of a hardenability resin composition to a value of 10 - 100,000 mPa·s (measurement temperature of 25 **) within the limits.

[0055]** Although it is not restricted, after it coats a substrate especially with a curing method of a curing method hardenability resin composition by various methods and it forms a coat, for example, it is preferred to irradiate with and stiffen radiation (photopolymerization reaction of reactive diluent). Thus, as radiation with which it irradiates to a coat, infrared rays, visible light, ultraviolet rays, a far ultraviolet ray, X-rays, an electron beam, alpha rays, a beta ray, a gamma ray, etc. can be mentioned, for example. When a radiation-initiated-polymerization initiator contains in a constituent which constitutes a coat like a 1st embodiment, it is preferred that the radiation-initiated-polymerization initiator concerned irradiates with radiation which has sensitivity. A dose of radiation can be suitably set up according to a kind of light source, thickness of a coat, etc.

[0056]When a cross-linking functional group content copolymer and a cross-linking compound contain into a hardenability resin composition of this invention, while irradiating with radiation to a coat of the hardenability resin composition concerned, it is preferred to heat the coat concerned. Thereby, a reaction (crosslinking reaction) of a cross-linking functional group content copolymer and a cross-linking compound can be promoted. Here, heat-treatment of a coat may be performed to any before and after radiation irradiation, and it may carry out simultaneously with radiation irradiation. As a heat-treatment means of a coat, oven etc. can be used, for example, content of a cross-linking functional group content copolymer in a constituent and a cross-linking compound, a kind of substrate, etc. can respond as heating

conditions, and it can set up suitably.

[0057] As a substrate with which a hardening layer is formed, plastics base material; glass base material; metal base; wood, such as polycarbonate resin, an acrylic resin, styryl resin, arylate resin, and norbornene system resin, etc. are mentioned, for example. As a coating method of a hardenability resin composition, For example, a method of using various coaters, such as a spin coater, a curtain coating machine, and a roll coater (the desirable viscosity range of a constituent: 1 - 10,000 mPa-s); A screen printing device, How (the desirable viscosity range of a constituent: 1 - 100,000 mPa-s) to use various printers, such as a gravure printing device and offset printing equipment; a dipping method (the desirable viscosity range of a constituent: 1 - 1,000 mPa-s) etc. are mentioned.

[0058]** It is preferred to make a glass transition point of a hardening layer of a glass transition point hardenability resin composition into a value within the limits of 40-90 **. This reason is because heat resistance and a mechanical strength of a hardening layer may fall if a glass transition point will be less than 40 **, and is for a case where adhesion power to a substrate declines to arise on the other hand, if a glass transition point exceeds 90 **. Therefore, since balance with the heat resistance of a hardening layer or adhesion is better, it is more preferred to make a glass transition point of a hardening layer into a value within the limits of 50-85 **, and it is still more preferred to consider it as a value within limits which are 60-80 **. The glass transition point of a hardening layer can conduct differential scanning thermometric analysis (DSC), and can compute it among nitrogen from a change point of specific heat obtained when it heats with 10 ** the heating rate for /as an example.

[0059] In a hardening layer obtained from a hardenability resin composition, although one glass transition point is obtained (refer to [drawing 4](#)), this is usually considered because a hardenability resin composition of this invention has the good compatibility of a hexafluoropropylene copolymer and alpha-fluoro acrylate monomer. That is, a glass transition point of the polymer A1 used with the hexafluoropropylene copolymer 1, for example, an example mentioned later, is usually within the limits of 0-40 ** (refer to [drawing 5](#)). On the other hand, a glass transition point of a polymer of alpha-fluoro acrylate monomer, for example, a trifluoroethyl alpha-fluoro acrylate monomer independent, is within the limits of 100-120 **. Therefore, although a hexafluoropropylene copolymer and alpha-fluoro acrylate polymer dissolve uniformly that the number of glass transition points of a hardening layer is one and it has not joined together chemically, it is thought that one glass transition point appears.

[0060] Therefore, such a glass transition point can be easily adjusted in conformity with a following formula.

$1/T_p = w_H/T_H + w_F/T_F$: A glass transition point of a hardening layer

(absolute temperature)

T_H : A glass transition point of a hexafluoropropylene copolymer

(absolute temperature)

T_F : A glass transition point of alpha-fluoro acrylate polymer (absolute temperature)

w_H : A weight fraction of a hexafluoropropylene copolymer (%)

w_F : A weight fraction of alpha-fluoro acrylate polymer (%)

[0061]However, depending on a kind of addition ingredient of a hardenability resin composition, two or more glass transition points may be obtained in a hardening layer. In that case, what is necessary is just to adjust a kind of the mixing ratio, a hexafluoropropylene copolymer, or alpha-fluoro acrylate monomer so that it may become a value within the limits of 40-90 ** about a value of a high glass transition point.

[0062][A 2nd embodiment] A hexafluoropropylene copolymer in which a 2nd embodiment includes a siloxane bond, It is a hardenability resin composition containing alpha-fluoro acrylate monomer, the alpha-fluoro acrylate monomer concerned, a copolymerizable ethylenic unsaturated compound (an ethylenic unsaturated compound may only be called hereafter.), and a radiation-initiated-polymerization initiator. Thus, by including ethylenic unsaturated compounds other than alpha-fluoro acrylate monomer, values, such as viscosity of a hardenability resin composition, a refractive index of a hardening layer obtained, adhesion power, a mechanical strength, can be adjusted easily. In the following explanation, an ethylenic unsaturated compound which is the feature of a 2nd embodiment shall be explained to a center, and suppose that it is the same as that of a 1st embodiment about other ingredients.

[0063](1) A kind alpha-fluoro acrylate monomer and a copolymerizable ethylenic unsaturated compound are compounds which carry out addition condensation that an activity energy line is irradiated under existence of a photopolymerization initiator or nonexistence, or by being heated under existence of a thermal polymerization initiator. As an example of such an ethylenic unsaturation polymerization nature compound, Alpha olefins, such as ethylene, propylene, and isobutene; Styrene, Alpha-methylstyrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, p-tert-butylstyrene, diisopropenylbenzene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene, 1,1-diphenylethylene, p-methoxy styrene, N,N-dimethyl- p-aminostyrene, N,N-diethyl- p-aminostyrene, Vinyl aromatic compounds, such as vinylpyridine and vinylimidazole; (meta) Acrylic acid, Carboxyl containing compounds, such as crotonic acid, maleic acid, fumaric acid, and itaconic acid; Methyl (meta) acrylate, Ethyl (meta) acrylate, propyl (meta) acrylate, isopropyl (meta) acrylate, Butyl (meta) acrylate, isobutyl (meta) acrylate, tert-butyl (meta) acrylate, Pentyl (meta) acrylate, amyl (meta) acrylate, isoamyl (meta) acrylate, hexyl (meta) acrylate, heptyl (meta) acrylate, octyl (meta) acrylate, Isooctyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, Nonyl (meta) acrylate, decyl (meta) acrylate, isodecyl (meta) acrylate, Undecyl (meta) acrylate, dodecyl (meta) acrylate, Lauryl (meta) acrylate, stearyl (meta) acrylate, Alkyl (meta) acrylate, such as isostearyl (meta) acrylate; Hydroxyethyl (meta) acrylate, Hydroxyalkyl (meta) acrylate, such as hydroxypropyl (meta) acrylate and hydroxybutyl (meta) acrylate; Phenoxyethyl (meta) acrylate, Phenoxy alkyl (meta) acrylate, such as 2-hydroxy-3-phenoxypropyl (meta) acrylate; Methoxy ethyl (meta) acrylate, Ethoxyethyl (meta) acrylate, propoxyethyl (meta) acrylate, Alkoxy alkyl (meta) acrylate, such as butoxyethyl (meta) acrylate and methoxy butyl (meta) acrylate; Polyethylene-glycol mono- (meta) acrylate, ethoxydiethylene-glycol (meta) acrylate, Methoxy polyethylene-glycol (meta) acrylate, phenoxypolyethylene-glycol (meta) acrylate, Polyethylene-glycol (meta) acrylate, such as nonylphenoxypolyethylene-glycol (meta) acrylate; Polypropylene-glycol mono- (meta) acrylate, Methoxy polypropylene-glycol (meta) acrylate, ethoxypolypropylene-glycol

(meta) acrylate, Polypropylene-glycol (meta) acrylate, such as nonylphenoxypolypropylene-glycol (meta) acrylate; Cyclohexyl (meta) acrylate, 4-butylcyclohexyl (meta) acrylate, dicyclopentani(metha) acrylate, JISHIKURO pentenyl (meta) acrylate, dicyclopentadienyl (meta) acrylate, Bornyl (meta) acrylate, isobornyl (meta) acrylate, Cycloalkyl (meta) acrylate, such as tricyclo deca nil (meta) acrylate; kind independent, such as benzyl (meta) acrylate and tetrahydrofurfuryl (meta) acrylate, or two or more sorts of combination can be mentioned.

[0064](2) Although an addition in particular of an addition ethylenic unsaturated compound is not restricted, it is preferred concretely to make this addition into a value of one to 1,000 weight section within the limits to alpha-fluoro acrylate monomer 100 weight section. If an addition of an ethylenic unsaturated compound will be less than one weight section, this reason, It is because the addition effect may not be acquired and is because the compatibility of a hardenability resin composition may fall, and a sediment may arise or a hardening reaction may become uneven on the other hand, if an addition of an ethylenic unsaturated compound exceeds 1,000 weight sections. Therefore, it is more preferred to make an addition of an ethylenic unsaturated compound into a value of two to 100 weight section within the limits to alpha-fluoro acrylate monomer 100 weight section, and it is still more preferred to consider it as a value of five to 50 weight section within the limits.

[0065][A 3rd embodiment] A 3rd embodiment of this invention is an antireflection film which consists of a hardenability resin composition explained by 1st and 2nd embodiments. This antireflection film should just be provided on a substrate, and can take various modifications as a layered product. Hereafter, an antireflection film (layered product) of a 3rd embodiment is explained concretely, referring to [drawing 1](#) - [drawing 3](#). [Drawing 1](#) is a sectional view of the layered product 14 containing the antireflection film 10 directly formed in substrate top 12, and [drawing 2](#) is a sectional view of the layered product 18 which made the hard court layer 16 intervene between the substrate 12 and the antireflection film 10. [Drawing 3](#) is a sectional view of the layered product 28 of multilayer structure which formed the substrate 12, the hard court layer 16, the 1st high refractive index layer 20, the 1st antireflection film 22, the 2nd high refractive index layer 24, and the 2nd antireflection film 26 one by one, and constituted them from the bottom.

[0066]Since the antireflection film 10 which consists of a hardenability resin composition explained by 1st and 2nd embodiments in the case of the layered product 14 shown in [drawing 1](#) can be directly formed on the substrate 12, composition is a monolayer, and is simple and, moreover, it can form with sufficient accuracy. Like the layered product 18 shown in [drawing 2](#), between the antireflection film 10 and the substrate 12, If the hard court layer 16 is made to intervene, adhesion power to the substrate 12 of the antireflection film 10 can be raised more, and it will originate in the mechanical property of the hard court layer 16, and endurance as the layered product 18 will improve more. For example, as for the hard court layer 16, it is preferred to constitute from materials, such as SiO₂, epoxy system resin, acrylic resin, and melamine system resin, and further, It is considering it as a value within the limits of 5-10 micrometers preferably [making the thickness into a value within the limits of 1-50 micrometers], and more preferably.

[0067] Like the layered product 28 shown in [drawing 3](#), besides the 1st and 2nd antireflection layers 22 and 26, It is also preferred to form the 1st and 2nd 50-200-nm-thick high refractive index layers 20 and 24 that have a value of a comparatively high refractive index, for example, a value of 1.5-2.0 (-) within the limits, in contact with the 1st and 2nd antireflection layers 22 and 26, respectively. Thus, the more outstanding acid-resisting effect can be acquired by forming the high refractive index layers 20 and 24 in contact with an antireflection layer of this invention, and moreover providing two or more layers. The antireflection layers 22 and 26 since the more outstanding acid-resisting effect is acquired when forming the high refractive index layers 20 and 24, It is preferred to make refractive index difference between the high refractive index layers 20 and 24 into a value more than 0.05 (-), it is more preferred to consider it as a value of 0.1-0.5 (-) within the limits, and it is still more preferred to consider it as a value of 0.15-0.5 (-) within the limits.

[0068] As shown in the layered products 18 and 28 of [drawing 2 - drawing 3](#), also when providing the hard coat layer 16, the high refractive index layers 20 and 24, or a primer layer (not shown), After coating a photoresist constituent of this invention on it, by irradiating with ultraviolet rays etc., the antireflection films 10, 22, and 26 which consist of a hardenability resin composition of 1st and 2nd embodiments can be formed easily. In that case, an antireflection film (antireflection layer) of this invention may be called including the high refractive index layers 20 and 24 which take part of responsibility for the acid-resisting effect.

[0069] A kind of substrate 12 in the layered products 14, 18, and 28 shown in [drawing 1 - drawing 3](#), Especially if it asks for the acid-resisting effect when light penetrates, it is not restricted, but glass, polycarbonate system resin, polyester system resin, or acrylic resin can be mentioned, for example. When the substrate 12 is glass, a lens part of a camera, a display section of television (CRT, LCD), or a windowpane is mentioned as a concrete layered product. In the case of the substrate 12 which consists of polycarbonate system resin, polyester system resin, or acrylic resin, a light filter in a liquid crystal display, etc. are mentioned.

[0070]

[Example] Hereafter, an example explains an embodiment of the invention still in detail. However, this invention is not restrained at all by these examples, unless the gist is exceeded. The part in an example and especially % show weight section and weight %, respectively, unless it refuses.

[0071] [Composition of a hexafluoropropylene copolymer]

(1) In carrying out polymer A1 Examples 1-5 and the comparative examples 1-4, the hexafluoropropylene copolymer as the polymer A1 was compounded. Namely, after nitrogen gas replaces enough the autoclave made from stainless steel with an electromagnetic-mixing machine with a content volume of 1.5 L., as shown in Table 1, As the ethyl acetate 600g, hexafluoropropylene (HFP), and a copolymerizable monomer as a solvent, 31.9 g of perfluoro (propylvinyl ether) (FPVE), 30.2 g of ethyl vinyl ether (EVE), and 15.8 g of hydroxyethyl vinyl ether (HEVE), as a nonionic reactive emulsifier -- ADEKA rear soap NE-30 (the Asahi Denka Kogyo K.K. make.) 30.0 g of emulsifiers I and whose s 9 and m are 30 in n in a general formula (3), After teaching

VPS-1001 (made by Wako Pure Chemical Industries, Ltd.) 1.28g, and 0.75 g of JIRAU roil peroxide (LPO) as azo content poly dimethylsiloxane, respectively and cooling to -50 °C with dry ice methanol, nitrogen gas replaced enough again.

[0072]Subsequently, temperature up was started after introducing 86.4 g of hexafluoropropylene in autoclave. The pressure in the time of the temperature in autoclave amounting to 60 °C showed 4.7 kgf/cm². Then, the reaction was continued under 25-hour stirring at 60 °C, when the pressure fell to 2.5 kgf/cm², autoclave was water-cooled, and the reaction was stopped. After reaching a room temperature, the unreacted monomer was emitted, autoclave was opened wide and the polymer solution was obtained. The obtained polymer solution was thrown into methanol, polymer was deposited, methanol washed, and the hexafluoropropylene copolymer (polymer A1) which performs vacuum drying at 50 °C, and includes a 129-g siloxane bond was obtained.

[0073]The obtained polymer A1 was adjusted using THF so that concentration might serve as a solution 0.5% of the weight, and the determination of molecular weight by gel permeation chromatography was performed. As a result, the number average molecular weight by polystyrene conversion was 76,800. Furthermore, the glass transition temperature (T_g) by DSC analysis and the fluorine contents by the alizarin complexone method were measured, respectively. The obtained result is shown in Table 1. A part for inorganic silica was measured from the analysis result of ¹H-NMR and ¹³C-NMR, an ultimate analysis result and fluorine contents, a hydroxyl value, and the residual weight after the calcination at 600 °C, and the rate of each monomer component which constitutes the polymer A1 from these measurement was determined. The result checked that it was a mole ratio of HFP/FPVE/EVE/HEVE/NE-30/(constituent by VPS-1001) = 39.7/9.7/33.8/13.6/1.1/2.1. Therefore, while the obtained polymer A1 certainly included the polysiloxane combination resulting from VPS-1001, it became clear that it taught only about NE-30 among each constituent in a copolymer, and the difference of a ratio and a constituent ratio had arisen.

[0074](2) In carrying out the polymer A2 comparative example 5, the hexafluoropropylene copolymer which does not include the siloxane bond as the polymer A2 was compounded. That is, in the presentation shown in Table 1, the polymer A2 as well as the polymer A1 was compounded. A number average molecular weight, fluorine contents, and glass transition temperature were measured like the polymer A1 per [which was obtained] polymer A2, respectively. The obtained result is shown in Table 1. The rate of each monomer component which constitutes the polymer A2 was similarly determined as the polymer A1. As a result, HFP/EVE = it checked that they were 49.8/50.2 of mole ratios.

[0075]

[Table 1]

			ポリマー-A1	ポリマー-A2
仕 込 み 量 ／ g	共重合成分	HFP	86.4	162.2
		FPVE	31.9	
		EVE	30.2	64.8
		HEVE	15.8	
		NE-30	30.0	
	重合開始剤	LPO	0.75	3.0
		VPS1001	1.28	
収量 (g)			129	184
重合転化率 (%)			75.7	83.9
数平均分子量 (×10 ⁴)			7.68	3.78
フッ素含量 (重量%)			49.8	51.3
ガラス転移点 (℃)			21.0	21.7

*VPS1001は、共重合成分としての機能もあるが、便宜上、重合開始剤として記載してある。

[0076]The cable address in Table 1 shows the following contents.
HFP : hexafluoropropylene FPVE : Perfluoro (propylvinyl ether)
EVE : ethyl vinyl ether HEVE : Hydroxyethyl vinyl ether VPS-1001 :
Azo content poly dimethylsiloxane (the molecular weight of 80,000 and
a polysiloxane portion is the Wako Pure Chemical Industries, Ltd.
make, and a number average molecular weight is about 10,000)
NE-30 : Nonionic reactive emulsifier NE-30 (made by Asahi Denka
Kogyo K.K.)

LPO : JIRAU roil peroxide [0077][Composition of alpha-fluoro
acrylate monomer] 1N sodium hydroxide solution 600mL which
capacity accommodated in the container of 2L, 42 g of methyl-alpha-
fluoro acrylate was agitated to the mixed solution which consists of
tetrahydrofuran 600mL and the p-methoxy phenol 0.08g for 4 hours,
and was made to react to it after being dropped under ice-cooling. The
obtained reaction mixture was condensed on condition of the oil bath
temperature of 30 **, and decompression degree 150mmHg. Then, after
adding 1N chloride 700mL slowly and making acidity or alkalinity of a
water layer into acidity, it extracted by methylene chloride 400mL, and
the organic layer was obtained. Subsequently, it filtered, after drying an
organic layer with anhydrous magnesium sulfate. The obtained filtrate
was condensed and 28.8 g of alpha-fluoroacrylic acid was obtained as a
white solid. It was slowly dropped at the mixed solution which consists
of obtained alpha-fluoroacrylic acid 24g, 26.5 g of trifluoroethanol and
the p-methoxy phenol 0.01g, and the methylene chloride 84.0g, ice-
cooling the concentrated sulfuric acid 52.1g. It agitated after the end of
dropping, heating by a 40 ** oil bath. Ice water 500mL was added
slowly 20 hours afterward, taking out and carrying out the ice water of
the reactor from an oil bath. This was extracted 3 times by methylene
chloride 300mL, and the organic layer was obtained. Saturated sodium
bicarbonate solution and a salt solution washed this organic layer,
respectively, and it filtered, after drying with magnesium sulfate
further. The obtained filtrate was condensed, distillation under reduced
pressure refined, and 23g of trifluoroethyl alpha **FURUORO acrylate
was obtained. Yield was 86%.

[0078][Example 1] 10.0 g of hexafluoropropylene copolymers (A1) which include the obtained siloxane bond as shown in Table 2, And IRGACURE 184 which is a radiation-initiated-polymerization initiator The hardenability resin composition was obtained by agitating 3.0 g on a room temperature and the conditions of 2 hours using a mixer with a non-solvent, after making it dissolve into the trifluoroethyl alpha **FURUORO acrylate 90g, respectively. (1) radiation-curing nature and (2) spreading nature were evaluated about the obtained hardenability resin composition (non-solvent). (3) transparency and (4) refractive indices were measured about the hardening layer formed from the hardenability resin composition. The result obtained, respectively is shown in Table 2.

[0079](1) On the glass plate cut by 20x30 cm of radiation-curing nature angle, coating of the hardenability resin composition was carried out in bar coater, and the coat of 200 micrometers of thickness was formed. Subsequently, so that a light exposure may serve as 300 mJ/cm² (irradiation time 3 seconds), 600 mJ/cm² (irradiation time 6 seconds), and 900 mJ/cm² (irradiation time 9 seconds) on 25 ** conditions among nitrogen, respectively. It irradiated with ultraviolet rays using the conveyor type high-pressure mercury lamp (2 kW) by ORC Manufacturing Co., Ltd., and the hardening layer was formed. About the obtained hardening layer, surface tackiness was measured by finger touch and the following standards estimated the radiation-curing nature (photoresist) of the hardenability resin composition.

O There is no surface tackiness of a hardening layer after :300 mJ/cm² exposure.

O There is no surface tackiness of a hardening layer after :600 mJ/cm² exposure.

** : There is no surface tackiness of a hardening layer after 900 mJ/cm² exposure.

x : There is surface tackiness of a hardening layer after 900 mJ/cm² exposure.

[0080](2) The hardenability resin composition was applied to 1-micrometer thickness by the dip coater, to the polycarbonate board of spreading nature 2 mm in thickness, and a size 10-cm angle, using the high-pressure mercury lamp, it exposed in nitrogen so that a light exposure might serve as 900mJ, and the hardening layer was obtained to it. About the obtained hardening layer, the existence of spreading unevenness was judged on the following standard by viewing, and spreading nature was evaluated.

O : spreading unevenness is completely nothing.

** : There is spreading unevenness slightly and it is **.

x : There is spreading unevenness and it is **.

[0081](3) On the glass plate cut by 20x30 cm of transparency angle, coating of the hardenability resin composition was carried out in bar coater, and the coat of 200 micrometers of thickness was formed. Subsequently, under nitrogen, on 25 ** conditions, it irradiated with ultraviolet rays using the conveyor type high-pressure mercury lamp mentioned above, and the hardening layer was formed so that it might become 900 mJ/cm² (irradiation time 9 seconds). Viewing estimated transparency on the following standard about the obtained hardening layer.

O : -- transparence ** : -- a little -- nebula x : -- nebula [0082](4) Coating of the hardenability resin composition was carried out to the glass plate

cut by the refractive-index angle of 20x30 cm in bar coater, and the coat of 200 micrometers of thickness was formed. Subsequently, under nitrogen, on 25 °C conditions, it irradiated with ultraviolet rays using the conveyor type high-pressure mercury lamp mentioned above, and the hardening layer was formed so that it might become 900 mJ/cm² (irradiation time 9 seconds). The refractive index was measured on conditions with a measurement temperature of 25 °C about the obtained hardening layer using the Abbe refractive-index meter.

[0083][Examples 2-3] As shown in Table 2, the hardenability resin composition (non-solvent) was manufactured like Example 1, respectively except having replaced with and composed the kind and addition of alpha-fluoro acrylate. And radiation-curing nature and spreading nature were evaluated per [which was obtained] hardenability resin composition, and transparency was evaluated like Example 1 about the hardening layer obtained further. The obtained result is shown in Table 2.

[0084][Examples 4-5] As shown in Table 2, while replacing the kind and addition of alpha-fluoro acrylate with, the hardenability resin composition (solvent use) was manufactured like Example 1, respectively except having added and composed the solvent. And transparency and a refractive index were evaluated like Example 1 per [which was obtained by evaluating radiation-curing nature and spreading nature per / which was obtained / hardenability resin composition] hardening layer. Reflectance and adhesion were further evaluated as follows about the obtained hardening layer. The obtained result is shown in Table 2.

[0085](5) After applying a hardenability resin composition in 1-micrometer thickness by a dip coater on the polycarbonate board of reflectance 2 mm in thickness, and a size 10-cm angle, using the high-pressure mercury lamp, bottom of nitrogen atmosphere 900 mJ/cm² was exposed, and the antireflection film was formed. The rear face of this polycarbonate board was made to apply and dry a lusterless black spray (trade name: quick-drying acryl lacquer spray lusterless black, product made from can PEAPIO). The reflectance in the wavelength of 550 nm was measured by making this into a test portion using the spectrophotometer with a 60 mmphi integrating sphere (Hitachi Type U-3410).

[0086](6) After applying a hardenability resin composition in 1-micrometer thickness by a dip coater on measurement 2 mm in thickness of adhesion, and the polycarbonate board of a size 10-cm angle, bottom of nitrogen atmosphere 900 mJ/cm² was exposed with the high-pressure mercury lamp, and the antireflection film was formed. The surface of the hardening layer was rubbed by having made this into the test portion using KIMUWAIPU (made in ten-section Kimberley), and the following standards estimated the adhesion (abrasion-proof nature) of the antireflection film to a polycarbonate board.

O : there is neither exfoliation of a coat nor generating of a crack.

x: Exfoliation arises in a part of coat, or a muscle-like crack occurs in a film surface.

[0087][Comparative examples 1-3] The hardenability resin composition (non-solvent) was manufactured like Example 1, respectively except having formed using fluoro acrylate other than alpha-fluoro acrylate, as shown in Table 2. And radiation-curing nature and spreading nature were evaluated per [which was obtained] hardenability resin

composition, and transparency, a refractive index, and reflectance were evaluated like Example 1 about the hardening layer obtained further.

The obtained result is shown in Table 2.

[0088][Comparative example 4] The hardenability resin composition (solvent use) was manufactured like Example 4, respectively except having formed using fluoro acrylate other than alpha-fluoro acrylate, as shown in Table 2. And radiation-curing nature and spreading nature were evaluated per [which was obtained] hardenability resin composition, and transparency, a refractive index, and reflectance were evaluated like Example 1 about the hardening layer obtained further.

The obtained result is shown in Table 2.

[0089]

[Table 2]

		実施 例 1	実施 例 2	実施 例 3	実施 例 4	実施 例 5	比較 例 1	比較 例 2	比較 例 3	比較 例 4	比較 例 5
(A)	ポリマー A1	10	10	35	50	50	10	10	30	50	
	ポリマー A2										50
(B)	ARF3F	90		45	50	36					50
	ARF4F		90								
(C)	3F						90			50	
	8F							90	70		
	NP-A			20		14					
(D)	Irg.184	3.0	3.0	3.0	1.5	1.5	3.0	3.0	3.0	1.5	1.5
(E)	MIBK				1900	1900				1900	1900
(1)放射線硬化性		◎	○	◎	◎	◎	△	×	×	△	◎
(2)塗布性		△	△	△	○	○	△	△	△	×	○
(3)透明性		○	○	○	○	○	△	×	×	×	○
(4)屈折率		1.404	1.408	1.429	△	△	白濁	白濁	白濁	△	△
(5)反射率		△	△	△	1.1	1.5	△	△	△	白濁	1.1
(6)密着性		△	△	△	○	○	△	△	△	×	×

*表中、(白濁)は硬化膜が白濁しており、測定不可であることを示す。

[0090]The cable address in Table 2 shows the following contents. An ingredient (A) expresses a hexafluoropropylene copolymer including a siloxane bond among Table 2, An ingredient (B) expresses alpha-fluoro acrylate, an ingredient (C) expresses fluoro acrylate other than alpha-fluoro acrylate, an ingredient (D) expresses a polymerization initiator, and the ingredient (E) expresses the solvent further.

ARF3F : Trifluoroethyl alpha-fluoro acrylate ARF4F : 2,2,3,3-tetrafluoro propyl alpha-fluoro acrylate Irg.184 : 1-hydroxy-cyclohexyl-phenyl-ketone (made in Tiba Specialty Chemicals)

3F neopentyl glycol diacrylate : Trifluoroethyl acrylate 8F :

Octafluoropentyl acrylate NP-A : (MIBK made from Kyoeisha Fatty-

chemistry Industry: methyl isobutyl ketone) [0091]

[Effect of the Invention]According to the hardenability resin composition of this invention, with the combination of the hexafluoropropylene copolymer which has a siloxane bond, and alpha-fluoro acrylate monomer. Even if it did not use a solvent, good compatibility can be acquired specifically and the outstanding radiation-curing nature and spreading nature could be obtained. Therefore, it can be used as the antireflection film in a base material surface, an antifouling film, etc., and also the hardenability resin composition of this invention can be conveniently used as adhesives, encapsulant, or an optical fiber clad plate.

[0092]According to the hardening layer of this invention, it had the adhesion outstanding to the substrate, and the outstanding transparency over a low refractive index and visible light could be acquired.

Therefore, the hardening layer of this invention can demonstrate the outstanding endurance and optical property, when it is used as an antireflection film, an antifouling film, etc.

[0093]According to the antireflection film of this invention, the characteristic as a hardening layer mentioned above being obtained and low reflectance, for example, 2% or less of value, came to be obtained. Since the antireflection film of this invention is constructing the bridge, its mechanical strength is high, and in order to make abrasion-proof nature and surface slidability (abrasion resistance) reveal, it has suitable hardness.

Since it has a siloxane bond and a fluorine group, being rich also in weatherability is expected.

[Translation done.]